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Integrated Refining of Balkhash Copper Mixtures by the Cyclone Method

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METHOD

[Kompleksnaya pererabotka Balkhashskikh mednykh shikht
tsiklonnym metodom]

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METHOD*

Introduction, Production Scheme, and Process Monitoring

The cyclone method of refining copper-bearing materials has been discussed quite thoroughly in the periodicals [1], and detailed information is available on the tests of the semicommercial cyclone unit in the Balkhash Mining and Metallurgical Combine in refining copper mixtures with different compositions [2, 3, 4].

However, these sources, while they contain sufficiently concrete and generalized data on the design and engineering indices for the cyclone unit, present what is incomplete and, in part, conjectural information on the behavior of the individual components of mixtures containing significant quantities of lead, zinc, and other (rare and dispersed) metals.

This article makes use of the results obtained with the semicommercial cyclone unit at the VNIITsvetmet [All-Union Scientific Research Institute of Nonferrous Metallurgy] in 1961-1962.

The work was performed in two stages:

- (a) preparations for balanced smelting, or cyclic smeltings;

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- (b) balanced smelting of Balkhash copper concentrates using a preheated air blast.

The cyclone unit at VNIITsvetmet has been described in reference [5], so we here shall include only those design changes that were incorporated in the unit as the work progressed.

First of all, coal dust heating, with introduction of the coal dust extended in the vertical direction, was used instead of mazut*. A faster-acting coal dust delivery screw conveyer was installed to eliminate pulsations in fuel combustion in the cyclone.

Figure 1 shows the engineering arrangements used to perform the work. We shall skip the detailed description of all the units shown in the figure and list here only the main dimensions of the cyclone; which are $D_{in} = 0.65$ m; $H_{in} = 1.1$ m; the settling chamber: $B_{in} = 2.0$ m; $L_{in} = 1.65$ m; and the air preheater: heating surface 76 m^2 .

The mixture was fed into the cyclone by a rotary-table feeder after first having been dried to a maximum moisture content of between 1 and 1.5%. Delivery of fuel to the cyclone, the coal dust mixed with primary air, was by a screw conveyer through an ejector (the dust was anthracite coal passed through a two-stage crushing process to provide 80 and 92 percent minus 0.2 mm and dried to a maximum moisture content of 0.5 to 1%).

The matte and slag obtained during the smelting process were removed through the corresponding tap holes in the settling chamber. The flue gases

* Translator's Note. Mazut is a Russian petroleum product remaining after the distillation of benzine and kerosine. It is a brownish-black liquid, and used largely as a fuel oil. Fay. Variant spellings include mazout, masut, and marsut.

flowed into the air preheater, the recuperator, through a short coupling and an air-cooled riser, after which they flowed through the dirty gas collector through a system of gas passages into wet electronic filters and, after scrubbing, were exhausted to atmosphere.

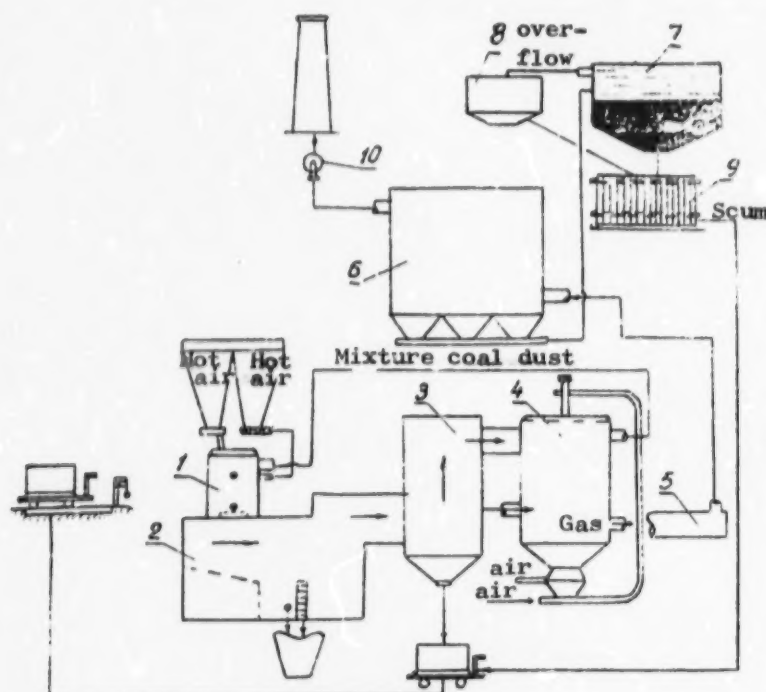


Figure 1. Diagram of the arrangement of the equipment in the cyclone unit. 1 - cyclone; 2 - settling chamber; 3 - dust chamber; 4 - recuperator; 5 - dirty gas collector; 6 - wet electronic filter; 7 - thickener (settler); 8 - collector; 9 - plate-and-frame press; 10 - smoke exhauster.

The process was monitored and regulated continuously throughout the balanced smeltings to follow mixture, coal dust, and air flows, the temperatures and vacuums at the different points along the circuit, and the composition of the waste gases. Gas dust content was checked periodically.

In addition, the matte and slag drawn off during each shift were subjected to chemical, and, when necessary, rational and petrographic, analyses.

The dust that precipitated in the flue was sampled and analyzed daily. The dust scrubbed out in the electronic filters, and solutions of the latter, were analyzed after each stage of the investigation.

Characteristics of Original Raw Material and Fuel

A Balkhash copper mixture, composed of a mixture of Balkhash and Dzhezkazgan copper concentrates, was used for the experiments.

Table 1. Chemical Composition of Balkhash Copper Mixture, %

Element Material	Cu	Pb	Zn	Fe	S	As	Sb	SiO ₂	CaO	Al ₂ O ₃
Mixture of first composition*	21.71	1.26	0.61	14.33	19.7	0.06	0.011	19.16	7.23	3.57

* The mixture contained cadmium, rhenium, and other metals, in addition to the elements listed.

The granular composition of the mixture was 2% plus 1.0 mm, 7.0% plus 0.2 mm, and 91.0% minus 0.2 mm.

Fuel composition by elements was W^P 0.75%, C^P 64.31%, A^P 23.88*, N^P 1.88%, O^P 4.38%, S^P 0.52%, V^2 26.0% [sic], Q_h^P = 6157 kcal/kg.

* The chemical composition of the ash part of the fuel (in %) was Fe 6.15, CaO 6.7, SiO₂ 52.5, and Al₂O₃ 28.5

Air Blast Balance Smelting of Balkhash Copper Concentrates (Mixtures)

Preparatory work, involving a series of test melts, preceded the balanced smelting of Balkhash mixtures.

The task of these melts was to determine the optimum technological

parameters of the process for subsequent work. At the same time, the reliability of operation of the individual components of the cyclone was checked, as was the stability of the process, the influence of temperature, and other factors, on separation of the products resulting from the smelting operation, on their composition, on the degree of elimination of lead, zinc, and other volatile and rare elements in the gas phase.

The result of the preliminary melts revealed that a temperature of between 1370° and 1400°C (in the settling chamber) was more or less satisfactory for cyclone smelting of Balkhash copper mixtures.

Moreover, the decisive influence of the gas phase on the distribution of the metals derived as smelting products was recognized. This was attributed to the fact that the basic reactions of the process took place in the cyclone chamber where the mixture components were found to be in suspension for the most part and subject to the simultaneous effects of the gas medium and the high temperature.

Also established was the fact that the composition of the flue gases should be CO_2 16.5 to 18.0%, CO 0.3 to 0.6%, and O_2 0.3 to 0.5%, in order to obtain a matte containing $50 \pm 2\%$ copper for a given mixture composition and for maximum elimination of the volatile metals.

Balanced smelting proper got underway after relative normalization of the conditions of the bath in the settling chamber and of the corresponding technological preparation. Conditions were:

- (1) mixture charge - 1000 kg/hr;
- (2) coal dust consumption - 300-330 kg/hr;

- (3) secondary air consumption - $2300-2400 \text{ nm}^3/\text{hr}$;
- (4) primary air consumption - $250-300 \text{ nm}^3/\text{hr}$;
- (5) temperature in settling chamber - 1400°C ;
- (6) temperature ahead of recuperator - 700°C ;
- (7) secondary air temperature - $450-500^\circ\text{C}$;
- (8) vacuum under the hood of the settling chamber - minus $0.5-1.0 \text{ mm H}_2\text{O}$;
- (9) height of liquid bath (matte + slag) prior to drawing off slag - maximum 600 mm ;
- (10) matte copper content - $50 \pm 2\%$.

Matte and slag were drawn off separately, but prior to so doing the matte was permitted to reach the $250-300 \text{ mm}$ level (to reach the overall level of $500-550 \text{ mm}$ for the bath was inadequate for any higher level).

Balanced smelting continued for 240 hours which 203 hours were smelting time.

Mean capacity of the cyclone, based on smelting time only, was 23.5 tons/day , or $7.1 \text{ t/m}^2/\text{day}$ when capacity was equated to the square of the settler section, and $64.4 \text{ t/m}^3/\text{day}$ when equated to the volume of the cyclone chamber.

Natural fuel consumption for smelting time was 303.66 kg/t of mixture, and 26.8% when converted to convention fuel.¹

The explanation for the high fuel consumption lies in (a) the small

1. The consumption of conventional fuel was $14-15\%$ for a 100-ton cyclone unit ($d_{\text{in}} = 1 \text{ m}$) (see Tsvetnyye metally [Nonferrous Metals], No. 3, 1960).

size of the cyclone unit, (b) low sulfur content of the mixture, (c) coal not ground fine enough, and (d) the high specific heat loss through the masonry of the settling chamber.

Air consumption was maintained at the specified level (based on a calculation of 7 nm³ per 1 kg of coal dust and 500 nm³ per one ton of mixture).

Tables 2 and 3 list the mode parameters and the results obtained during the period of balanced smelting.

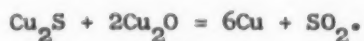
The atmosphere in the cyclone was close to neutral (CO₂ - 18.2%; CO - 0.39%; O₂ - 0.45%), but the SO₂ concentration in the flue gases was lower than expected (1.49-3.8%). This can be explained by the fluctuations that occurred in the quantities of sulfur in the mixture, as well as by the seepage of cold air into the settling chamber because of failure to comply with draw conditions, and this latter had a negative effect in particular on the magnitude of the dust carried off.

Matte composition, in terms of basic components, varied notably more than did the composition of the mixture, for example, but nevertheless the mean copper content obtained, 50.14%, confirmed the correctness of the working conditions selected, as well as the accuracy with which they were observed.

Slag, with respect to content of basic metals, copper, lead, zinc, was obtained such that it was close to that estimated in terms of total content when dumped. Only the quantities of silica, calcium oxide, and aluminum oxide, were higher than the original quantities (in the mixture),

and this can be explained by the passage into the melt of coal dust fuel ash and the eroded part of the masonry from the settling chamber.

Microscopic analysis developed the fact that the copper in the slags was primarily (60-70%) in finely dispersed metallic form (drop size was a maximum 0.02-0.03 mm), and, to a lesser degree in the form of sulfide. The metallic copper in all probability was obtained as a result of the following reaction



The following reaction also is possible in the mass of slag



The composition of the dust in the flue (based on data from analysis of daily samples) differed little from the original mixture in terms of copper, and the same was noted with respect to CaO and Al_2O_3 .

Rational analysis of the dusts (Table 2) showed that the basic compounds found in them were sulfates, with the percentage of these latter increasing from dust in the flue to the scum, inclusive. The percentage of copper sulfate (in terms of the total quantity of it in the particular dust) changed from 45% in the dust in the flue to 72% in the dust in the collector, for example. The copper sulfate in the scum can be as high as 95%.²

2. The oxidized copper of the scum is conventionally taken as sulfate because upon neutralization of the solution from the electronic filters by soda all of the copper sulfate is converted into cupric hydroxide.

Table 2. Rational Analysis of the Dusts Obtained During
the Balanced Smelting Period, %

Element, form of compound	Least smelting product	Flue dust	Dirty gas collector dust	Scum
Copper: total		16.48	13.29	19.88
sulfate		7.43	9.57	none
oxide		7.40	1.78	18.88
sulfide		0.43	0.25	0.58
ferrite, and others		4.12	1.72	0.38
Zinc: total		3.61	4.97	6.15
sulfate		0.13	1.71	0.07
oxide		0.24	1.54	5.20
sulfide		0.08	0.07	0.90
ferrite, and others		2.44	1.67	0.43
Lead: total		9.45	9.45	6.42
sulfate		8.43	6.57	0.81
oxide		0.22	0.70	5.20
sulfide		0.58	2.04	0.34
Iron, water-soluble		0.17	0.45	trace

The zinc found in the flue dust was primarily (67.6% of the total) in the form of ferrites, and was distributed almost equally among the sulfate, oxide, and ferrite forms in the dust in the collector. Zinc was present in the scum primarily in the oxide form, although it most probably was in the sulfate form prior to processing the solution with soda. The sulfate form was most characteristic of the lead from the beginning to the end of the

flue system, while 89.2% of the total Pb was sulfate in the dust in the flue, 69.4% in the dust in the collector, and 12.6% in the scum. At the same time, 81.0% of the lead entered the scum in oxide form. The reason for this is the same as in the case of the copper and zinc; that is, oxidized lead in the scum is of secondary origin.

The dust in the collector contained a significant quantity of lead sulfide, 21.6% of the total, something that was not characteristic of the other dusts. When analyzing the behavior of the basic metals as they moved along the gas path, one noted that it was determined unalterably by temperature conditions on the one hand, and on the other by the composition of the gas phase. Lead sulfate, for example, can form at the beginning and in the middle of the flue (where the temperature is 800°-400°C) and then can be propagated all along the flue.

The formation of sulfates of copper and zinc was observed primarily in the middle of the flue, where the temperature was below 500°C, but the concentration of sulfur trioxide was relatively high.

Ferrites of copper and zinc were characteristic of the beginning and middle of the flue. There evidently is a site along the dirty gas collector section where secondary sulfates (from the oxides of the metals and the SO_3) form. The formation of sulfates in the wet electronic filters (solutions) can be explained by the reaction between the oxides of the metals and the free sulfuric acid that resulted from the water washing of the electronic filters. Oxidized metals appeared in the scum, as mentioned above, because their sulfates, reacting with the calcined soda put into the solution to neutralize it, were converted into the corresponding hydroxides.

Table 3. Material Balance and Distribution of Basic Elements in the Products of Air Blast Cyclone Smelting of Balkhash Copper Concentrates (Mixtures).

Mixture ingredients and smelting products	Total quantity		Copper				Lead				Zinc				Iron			
			соль-жа-ние, %		колич-во, кг		соль-жа-ние, %		колич-во, кг		соль-жа-ние, %		колич-во, кг		соль-жа-ние, %		колич-во, кг	
	kg	% от веса шихты	a	b	c	d	a	b	c	d	a	b	c	d	a	b	c	d
Mixture of first composition	198402.0	100.0	21.71	43076	100.0	1.26	2505.6	100.0	0.61	1190.4	100.0	14.34	28440.5	100.0				
Total	198402.0	100.0	43076				2505.6				1190.4		28440.5					
Matte	81572.0	41.1	50.14	40903.4	94.96	0.35	288.2	11.5	0.20	163.1	13.7	22.17	18088.1	63.6				
Slag	96650.0	48.7	0.48	467.1	1.08	0.15	146.27	5.8	0.15	149.1	12.5	11.4	11025.0	38.8				
Flue dust	4779.0	2.4	17.89	854.2	1.98	10.98	524.81	20.9	4.57	216.83	18.2	7.85	375.2	1.3				
Dirty gas collector dust	8150.0	4.1	14.32	1167.0	2.71	10.81	881.5	35.2	3.75	305.6	25.7	6.44	524.8	1.8				
Scum*	5763.0	3.5**	19.55	1686.7	3.92	5.01	288.7	11.6	3.7	532.4	44.7	2.06	463.1	1.6				
	1182.3		10.19															
Total	198966.3	99.8		45078.4	104.65		2129.48	85.0		1367.0	114.8		30476.2	107.1				
Discrepancy	- 305.7	-0.8		+202.4	+4.65		- 376.12	-15.0		+176.6	+14.8		+235.7	+7.1				

* Extraction includes the components of scum-precipitation, sum from the neutralization of the solution from the electronic filter and of the solution precipitated prior to neutralization. The numerator is the mean content of components in the scums, the denominator the content of the corresponding metals in the solution, in g/liter.

** Included in the magnitude of scum yield are the soluble components of the fine fraction of dusts precipitated in the wet electronic filters (copper, zinc, and iron are included in the form of sulfides in order to simplify the metal).

*** The great imbalance in scum-formers is the result of the addition to them of the corresponding components from the ash part of the coal dust fuel.

4* The sulfur imbalance is negative. The entire discrepancy can be assigned to the gas phase without particular error.

Table 3 Continued

Mixture ingredients and smelting products	Sulfur				Silica				Calcium oxide				Aluminum oxide			
	соеп- жа- ние, %	количество, кг	извле- чение, %	соеп- жа- ние, %	соеп- жа- ние, %	количество, кг	извле- чение, %	соеп- жа- ние, %	соеп- жа- ние, %	количество, кг	извле- чение, %	соеп- жа- ние, %	соеп- жа- ние, %	количество, кг	извле- чение, %	
Products	b	c	d	b	c	d	b	c	d	b	c	d	b	c	d	
Mixture of first composition	19.7	39082.3	100.0	19.16	38020.2	100.0	7.23	14345.6	100.0	3.57	7083.0	100.0				
Total		39082.3			38020.2			14345.6			7083.0					
	Produced															
Matte	23.96	15546.1	50.0										0.15	122.4	1.7	
Slag	0.6	579.9	1.5	47.48	45882.1	120.7	18.52	18281.4					7.91	7641.0	107.7	
Flue dust	10.44	498.9	1.2	12.2	583.28	1.5	7.28	348.13					3.16	172.0	2.4	
Dirty gas collector dust	12.11	986.9	2.6	9.01	434.3	1.1	5.77	470.2					2.66	243.4	3.4	
Scum*	9.9	626.0	1.8	5.73	330.2	0.9	1.93	111.2					3.13	180.4	2.6	
	7.0															
Total		22237.8			47229.88	123.2		19210.93	133.8		2359.2	116.1				
Discrepancy		-16844.5*		-	+9209.68***	+23.2		+4865.33***	+33.8		+1226.2***	+16.1				

Legend for Table 3:

a - % of mixture weight

b - content %

c - quantity, kg

d - extraction, %

The yield of smelting products, listed in Table 3, indicates that when conditions are such that quantities of matte and slag are normal, the dust yield is disproportionately higher (10% of the weight of the mixture). This too finds its explanation in the increased mechanical carry-over of the overdry mixture, in the fact that the sulfides of the metals are converted into heavier sulfates in the flue, and in the mixing into the dusts of substances (compounds of sodium remaining in the scum after neutralization of the solution) that are in no way related to the cyclone process. A detailed calculation showed that the actual mechanical carry-over of the mixture was 4.53%. Table 3 lists data on the distribution of the basic metals in terms of the smelted products.

It should be noted that the matte extraction indicated, 94.96%, does not include the return to the melt of the copper-containing reversible materials. The total copper extracted in the matte will be as high as 97-98% when the returns are included.

There are two factors, primarily, that can explain the transfer of the disproportionately large quantity of copper in the dust (as compared to the iron, calcium oxide, and silica): (1) the finely-dispersed particles of copper minerals (exceeding that specified during evacuation); and (2) the possible volatility of the copper sulfide at the high temperatures involved in the process, something that requires a special experimental check, however.

Extracted in the dust was 67.7% of the lead of a total extraction of lead in the smelted product of 85%. The discrepancy in the lead balance can be explained by the inaccuracy in analyses resulting from the comparatively

low lead concentration in the matte and in the slag, as well as in the original product.

The zinc was transferred in the dust, primarily (88.6%). Zinc content in the matte and slag was very low (0.15%). The reason for the heavy imbalance in zinc is the same as that given for lead.

The most characteristic rare metals contained in the Balkhash copper mixture were distributed as follows:

1. Cadmium, 94.8%, was carried in the gas phase, and of this 32.65% (absolute) was concentrated in the solutions from the wet electronic filters;

2. Rhenium was distributed primarily among two products, the matte (15.4%) and the gas phase (77%).

The calculation made for extraction of rhenium in the dust-gas phase did not include that remaining in the flue gases after the wet electronic filters. This had a negative effect on the magnitude of its extraction in the dust. The total rhenium extraction in the dust-gas phase was about 84% when the rhenium missing in the balance was included.

It should be noted that 92% of the total quantity of rhenium in the entrained dusts falls in the solution from the wet electronic filters.

Table 4 lists comparative data on the distribution of lead and zinc between smelted products for the different methods of processing the lead- and zinc-containing copper concentrates.

Despite the different methods of processing different types of copper ores, the general behavior pattern in the distribution of lead and zinc

between the smelted products points to a clear advantage of the cyclone method as compared to the others.

Table 4. Distribution of Lead and Zinc by Smelted Products, %

Name of product Type of smelting*	Matte		Slag		Dust	
	Pb	Zn	Pb	Zn	Pb	Zn
a Отражательная плавка медноцинковых концентратов Урала [6]	—	35 ÷ 40	—	55 ÷ 60	—	8 ÷ 12
b Отражательная плавка медных концентратов Джезказгана	55 ÷ 60	37 ÷ 40	18 ÷ 20	45 ÷ 50	—	8 ÷ 10
c Электроплавка медных концентратов Джезказгана [7]	83,6	83,0	5,5	22,4	10,9	14,6
d Циклонная плавка иртышских полнметаллических концентратов	20,7	25,0	2,3	10,5	77,0	64,5
e Циклонная плавка джезказганских медных концентратов	2,52	1,14	3,44	7,2	94,0	86,45
f Циклонная плавка балхашских медных шпат**	13,5	11,92	6,8	10,9	79,7	77,18

* The use of reversible materials (converter slag, and others) was envisaged in all typed of smelting except cyclone.

** Data on lead and zinc listed include imbalance in these metals (see Table 3).

Legend:

- a - Reflection smelting of Ural copper-zinc concentrates [6]
- b - Reflection smelting of Dzhezkazgan copper concentrates
- c - Electric smelting of Dzhezkazgan copper concentrates [7]
- d - Cyclone smelting of Irtyish semimetallic concentrates
- e - Cyclone smelting of Dzhezkazgan copper concentrates
- f - Cyclone smelting of Balkhash copper mixtures**

Doubts attributable to the fact that the cyclone method does not envisage the processing of the turnovers will, to a considerable degree, be dispersed if one considers that the converter slags produced when mattes from cyclone smelting are subjected to the Bessemer process cannot be rich in lead and zinc, and, consequently, cannot bring about any basic changes in the distribution of these metals in the basic process.

Processing any type of lead- and zinc-containing ore in a reflection furnace leads to the spreading of these metals into all the products and to their constant circulation within the limits of metallurgical production,

with the end result a reduction in the quality of the end product produced, and in that of copper in particular. The processing of a similar copper ore by the electrothermal method does not have these drawbacks.

Conclusions

1. The cyclone unit functions stably and reliably. Control of the installation and the cyclone smelting process can be readily regulated within broad limits.

The unit productivity, equated to the cyclone chamber, is $64.4 \text{ t/m}^3/\text{day}$, and $7.1 \text{ t/m}^2/\text{day}$ when equated to the hearth bottom of the settler when a preheated air blast is used during smelting.

2. The use of the cyclone smelting method to process copper ore results in composite and greater extraction of the valuable elements, including the rare metals and the metals dispersed in the gas phase (sublimates), than is the case when other methods are used.

3. Cyclone smelting dusts can be processed independently, providing for a more complete extraction from them of the valuable elements. At the same time, the total extraction of copper in the end product, black copper, is increased to at least 98%.

4. Observation of optimum parameters for the process, that is, the composition of the gas phase for a specified fuel-mixture-air ratio, makes it possible to obtain the matte and waste slag with the required copper content.

5. Wet (water washed) electronic filters are the devices needed in

the gas-scrubbing system to more completely trap the valuable elements,
including the rare metals, when the cyclone smelting method is used.

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